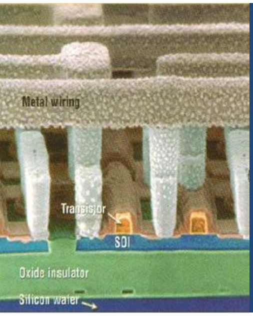
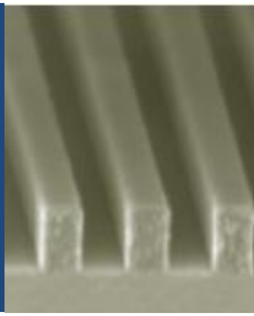


Development of DSA Approaches for Healing of LER and Shrinking of CD that are Compatible with Standard EUV Resists



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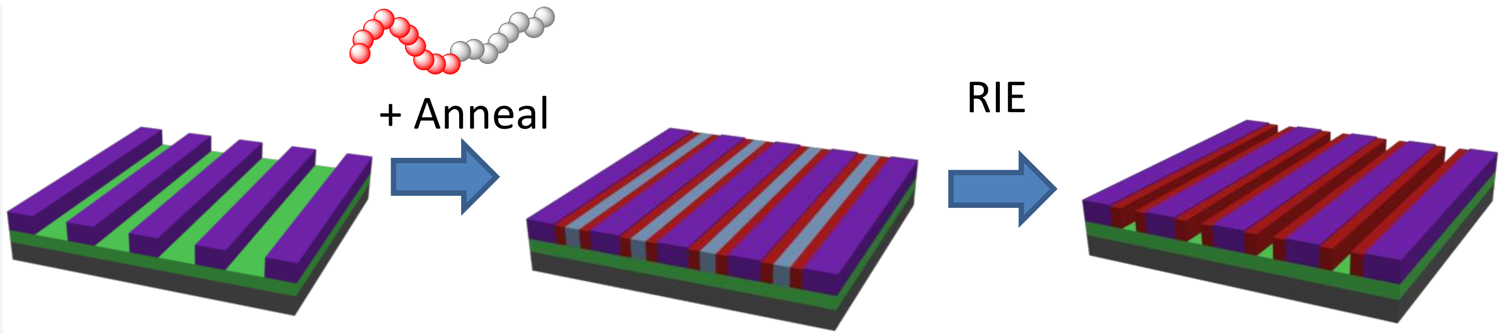
Motivation and Aims

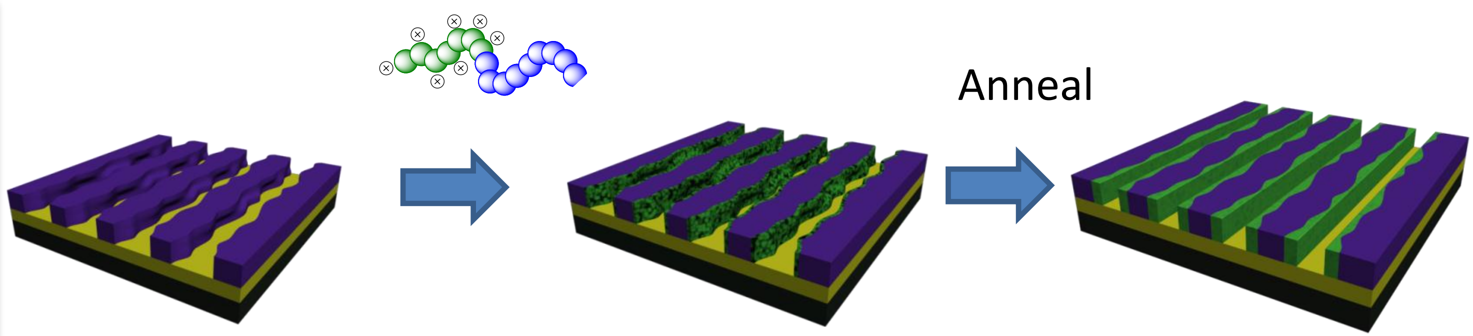
- Despite significant improvements, the ability to simultaneously achieve ITRS targets for resolution, sensitivity and LER remains elusive.
  - A number of resists can now achieve the resolution and sensitivity targets, but fall short when it comes to LER.
- UQ's Aim: To develop directed self assembly (DSA) materials and processes that can heal the LER of EUVL resists.

Block Copolymer (BCP) Healing of LER

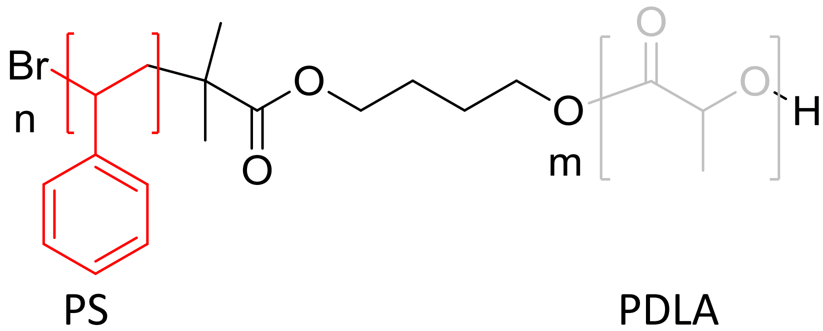
<u>Concept 1</u>: Deposition and patterning of block copolymer within features

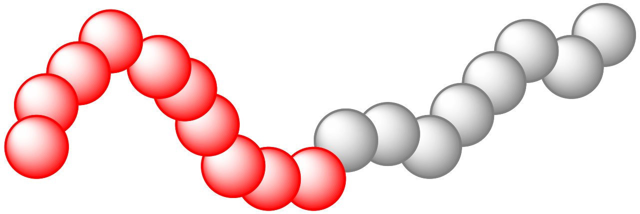


<u>Concept 2</u>: Coating of side wall features with block copolymer



Why PS-b-PDLA?





- PS-b-PDLA has favourable thermodynamic properties.
  - χ(298 K) = 0.217 – 0.233 [1]
    - Domain sizes of < 8 nm (pitch/L_0 <16 nm) are theoretically possible .
  - T_g values are below T_g values of most resist polymers.
  - PDLA block is easily degraded by hydrolysis.
  - Ohnishi parameters predict and our experiments show that PS block has a higher etch resistance than PLA.

BCP	χ_{AB}
PS-b-PMMA	0.041
PS-b-PDLA	0.217

Bigger χ is better

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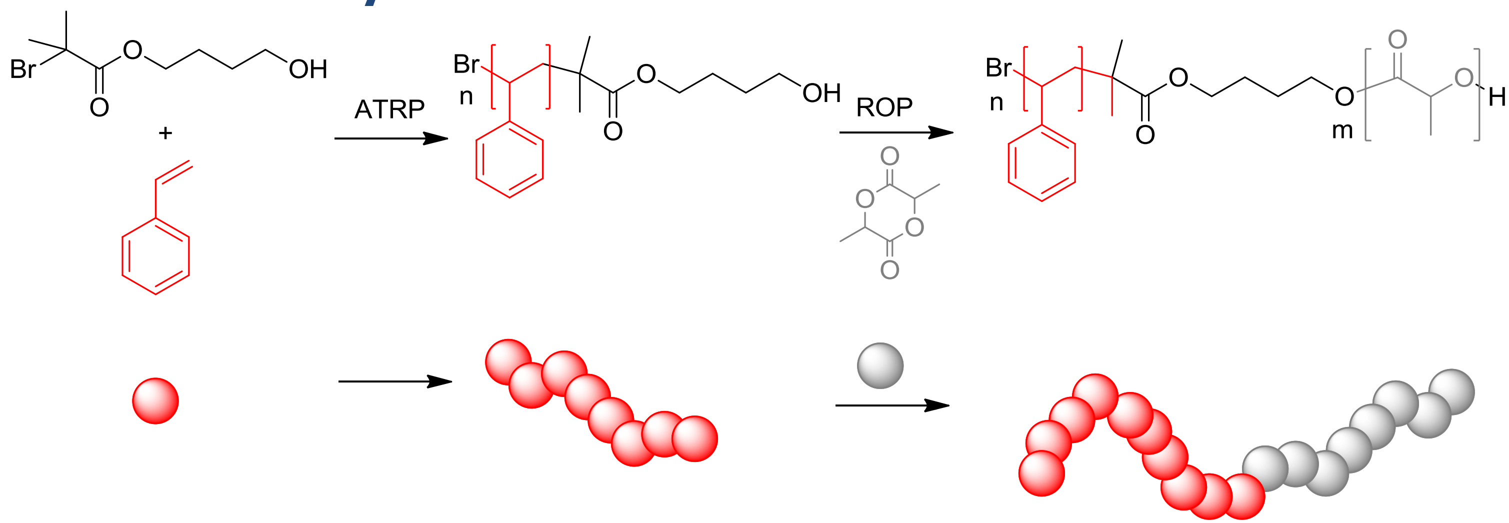
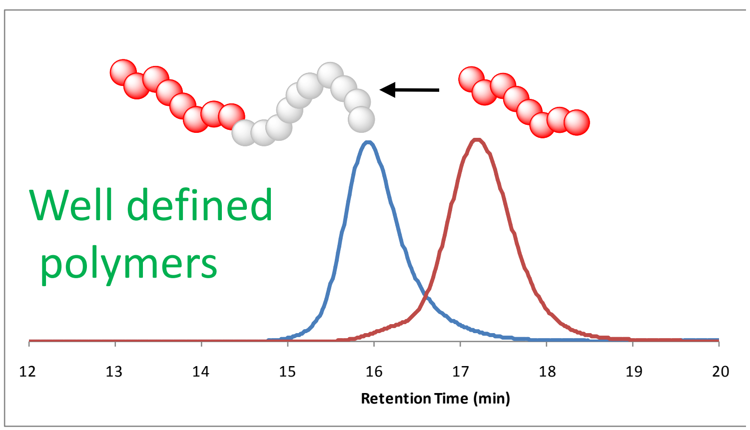
[1] Zalusky, et al. JACS 2002, 124, 12761.

Synthesis of PS-*b*-PDLA



Polymer Size Analysis

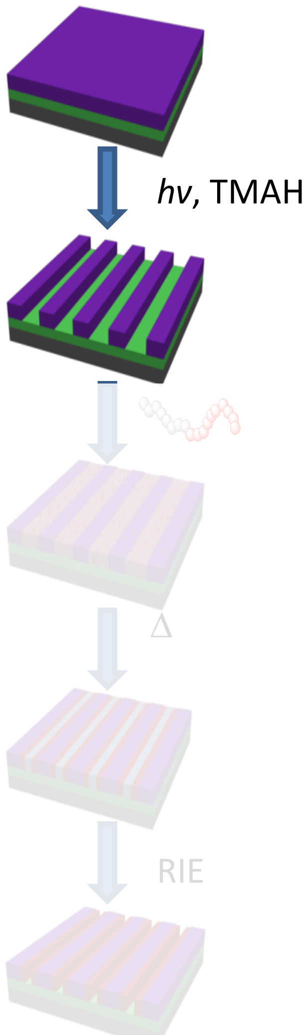
14.7 k 6.9 k

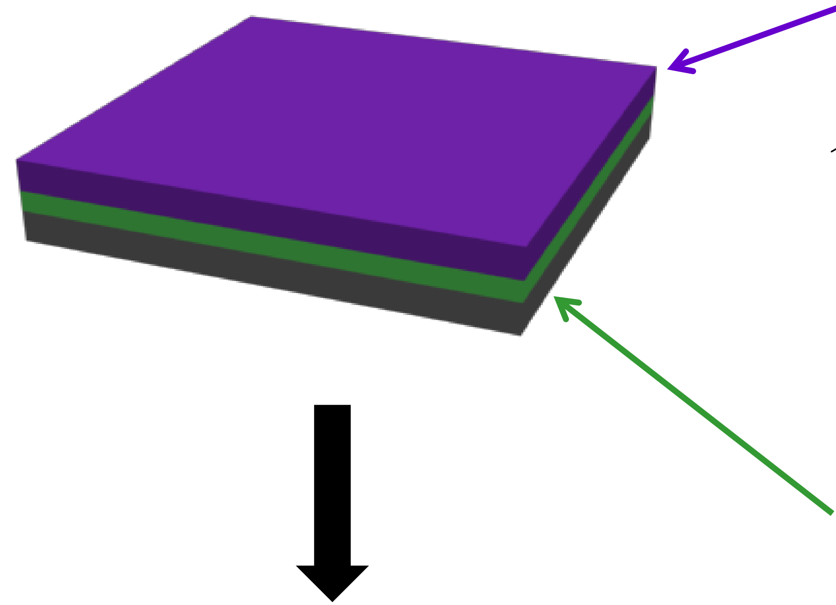


MW	vol % PDLA	PDI	χN	Bulk L_0 by SAXS (nm)	Bulk domain size by SAXS (nm)
12.0k	50	1.25	30.6	15.9	8.0
14.7k	48	1.14	37.0	16.5	8.3
16.5k	46	1.18	42.1	19.8	9.9
21.0k	48	1.25	53.6	21.3	10.7

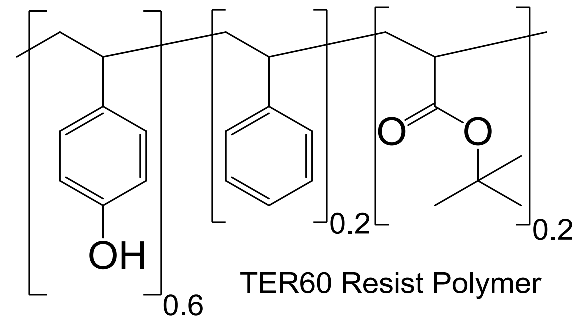
We have also developed variants that should be able to achieve smaller feature sizes (*i.e.* Predicted to have higher χ parameters).

EBL Patterning



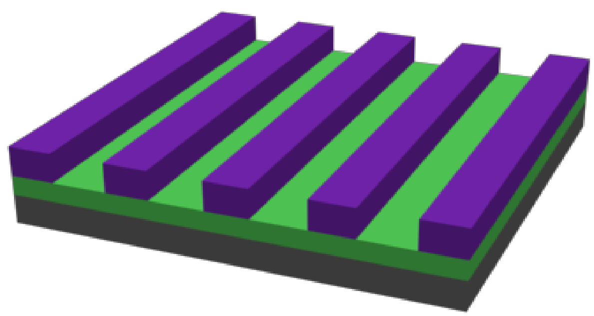


Resist:
PHOST based EUV resist



TER60 Resist Polymer

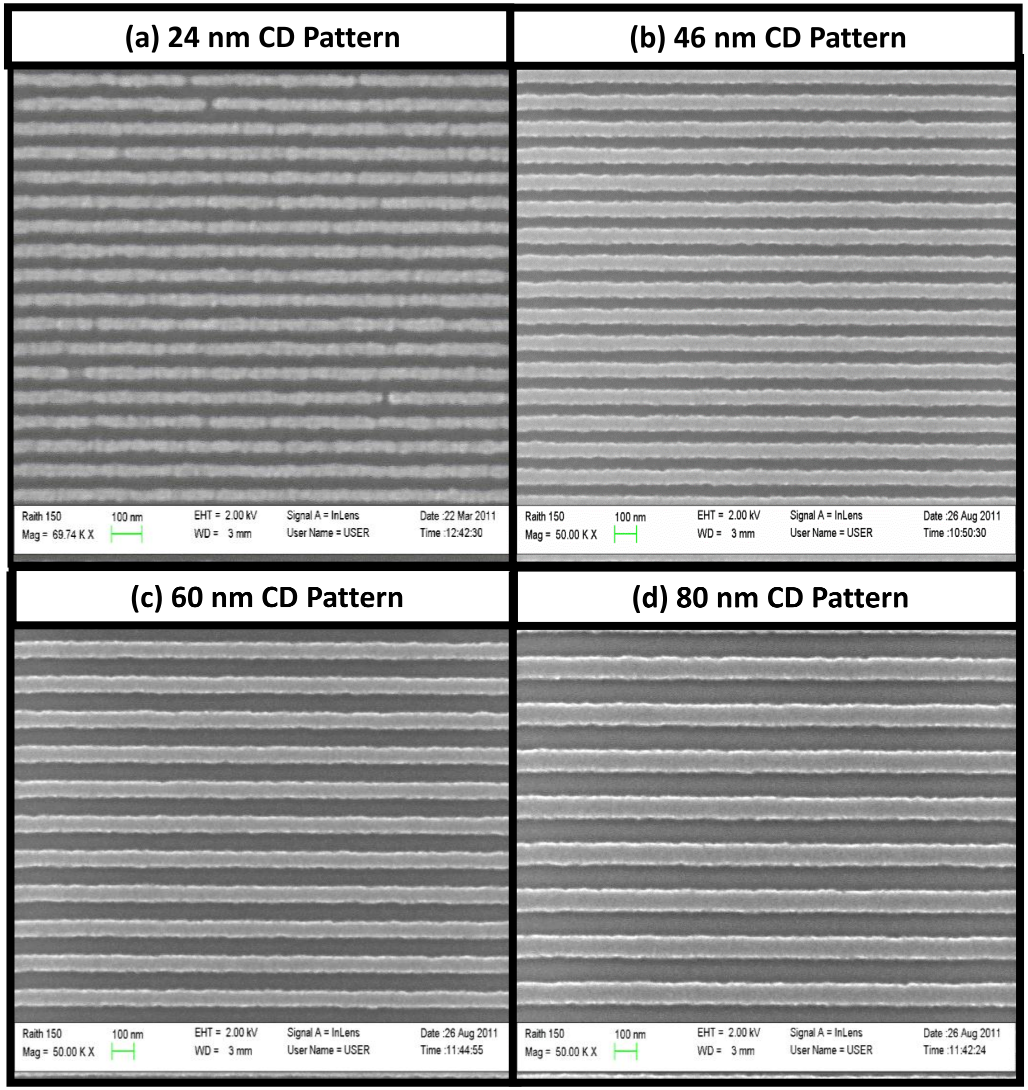
SEML: PMMA-r-PS (38 % PS)
or Brewer science underlayer



Developer: 2.38 % $TMAH_{(aq)}$

1. EUVL, thanks to Intel Corp.
    - Micro exposure tool (MET).
2. Electron Beam Lithography
    - JEOL 6610 EBL @ CMM, UQ.
    - Raith-150 @ ANFF-ACT, ANU.

Patterning Results



- PAB 95 °C, PEB 105 °C.
- Dose =
  - ~16 mJ/cm^2 (EUVL).
  - ~40 µC/cm^2 (20 kV EBL).
- LER = 4 - 7 nm.

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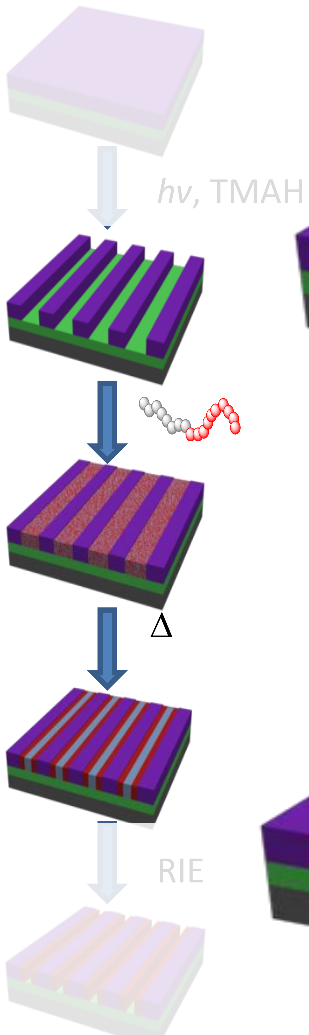
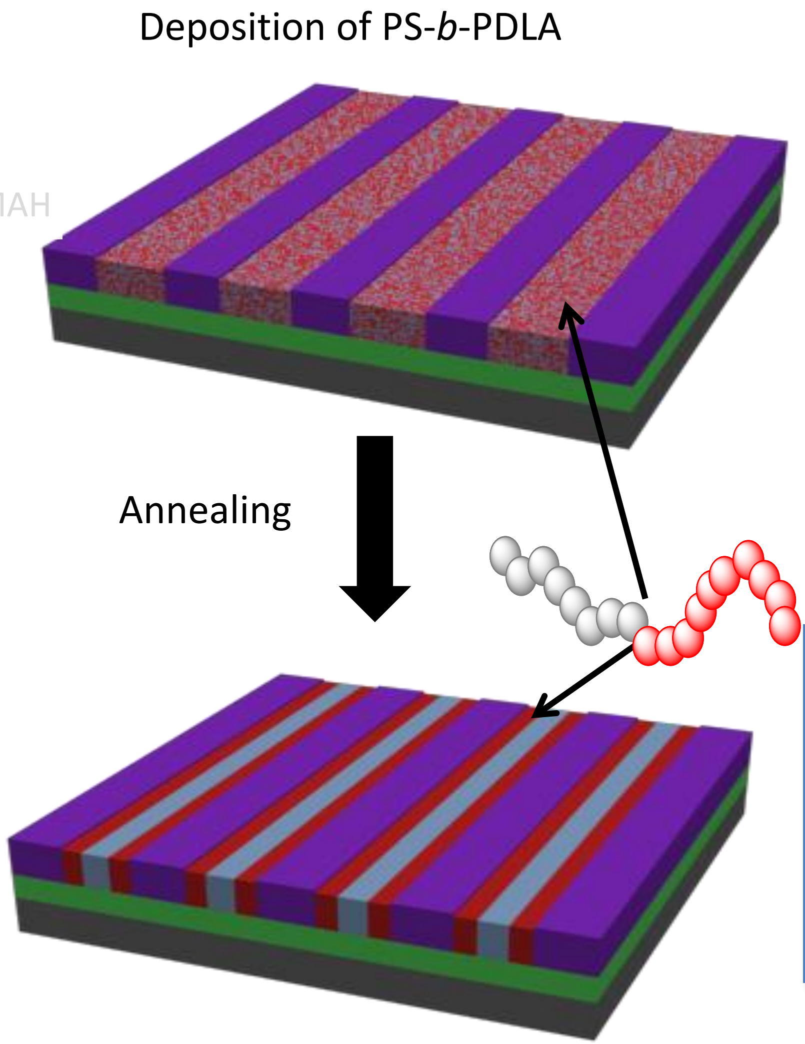
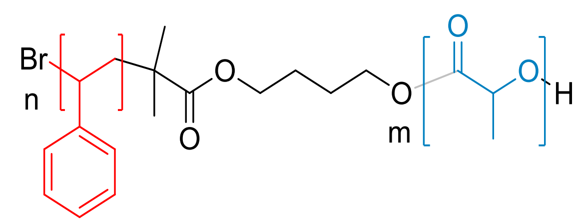
DSA - BCP Deposition and Annealing





Solvent for deposition of BCP is a non-solvent for the resist.

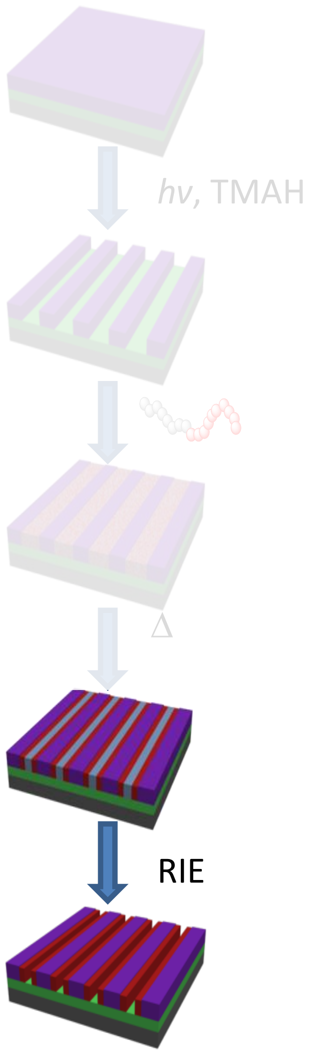
Polystyrene – *b* – poly(DL-lactide) or PS-b-PDLA

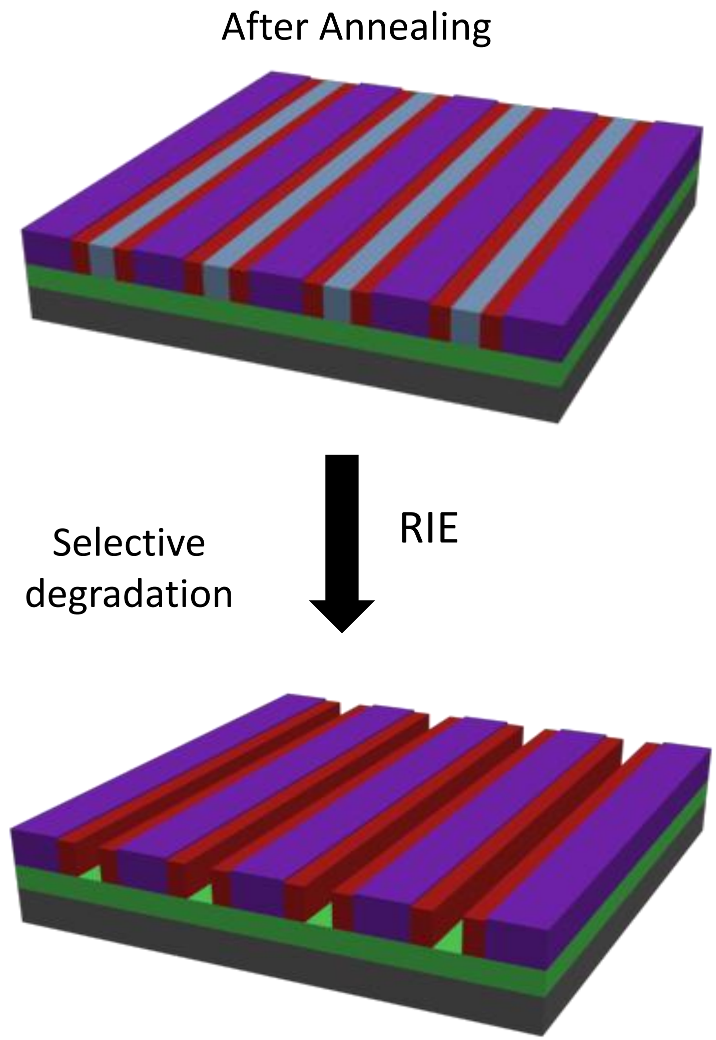


Annealing temperature = 100 °C

- Lower than T_g of resist (123 °C)
- Much lower than annealing temperature required for PS-*b*-PMMA (>180 °C)

Dry Etch of BCP





Etch Rate (nm/s)

Polymer	20 W, 5 sccm Ar 30 s etch
PS	**0.93**
PDLA	**3.6**
PMMA	**2.3**

Selectivity

Polymer	20 W, 5 sccm Ar 30 s etch
PS	**1**
PDLA	**4**
PMMA	**2.5**

Selectivity 1.6 x higher than PS-*b*-PMMA

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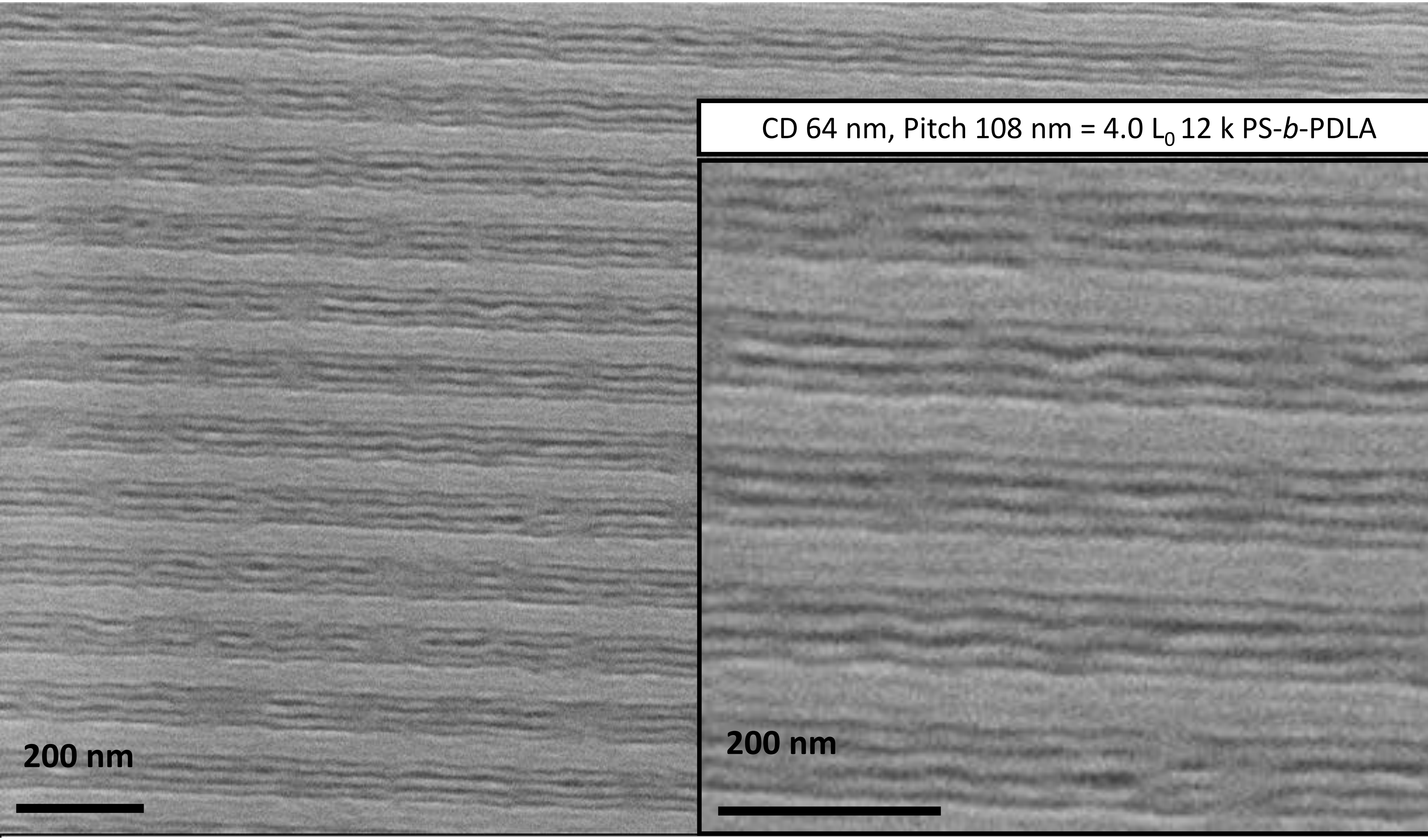
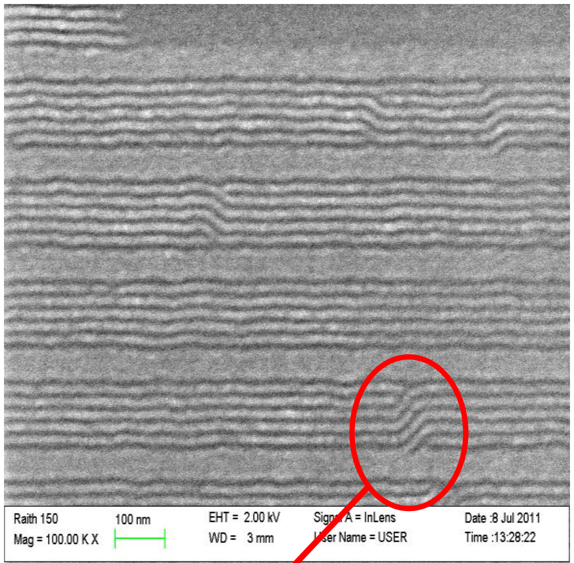
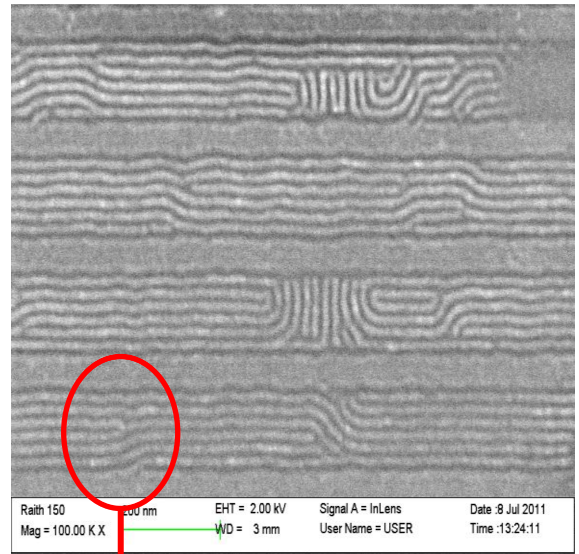
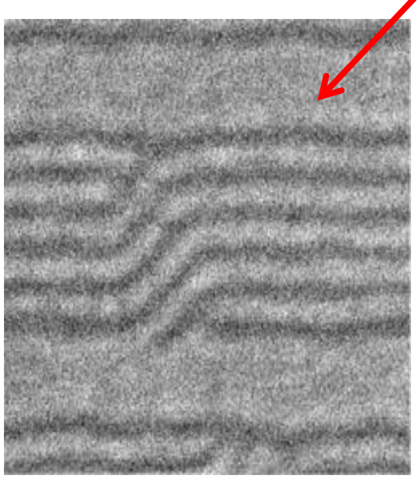
DSA Results (4× Pattern Multiplication, $4L_0$)



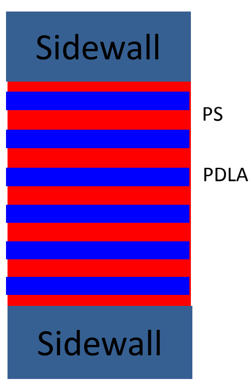
DSA Results ($6L_0$, $7L_0$)

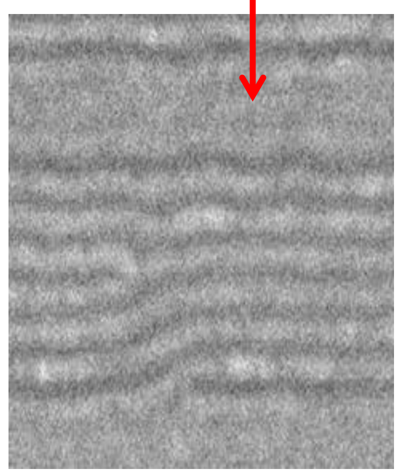




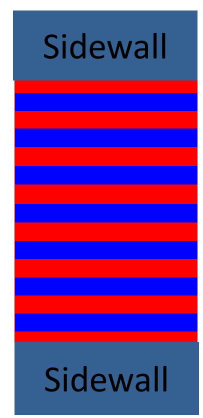


($6.5L_0$)





($7.5L_0$)

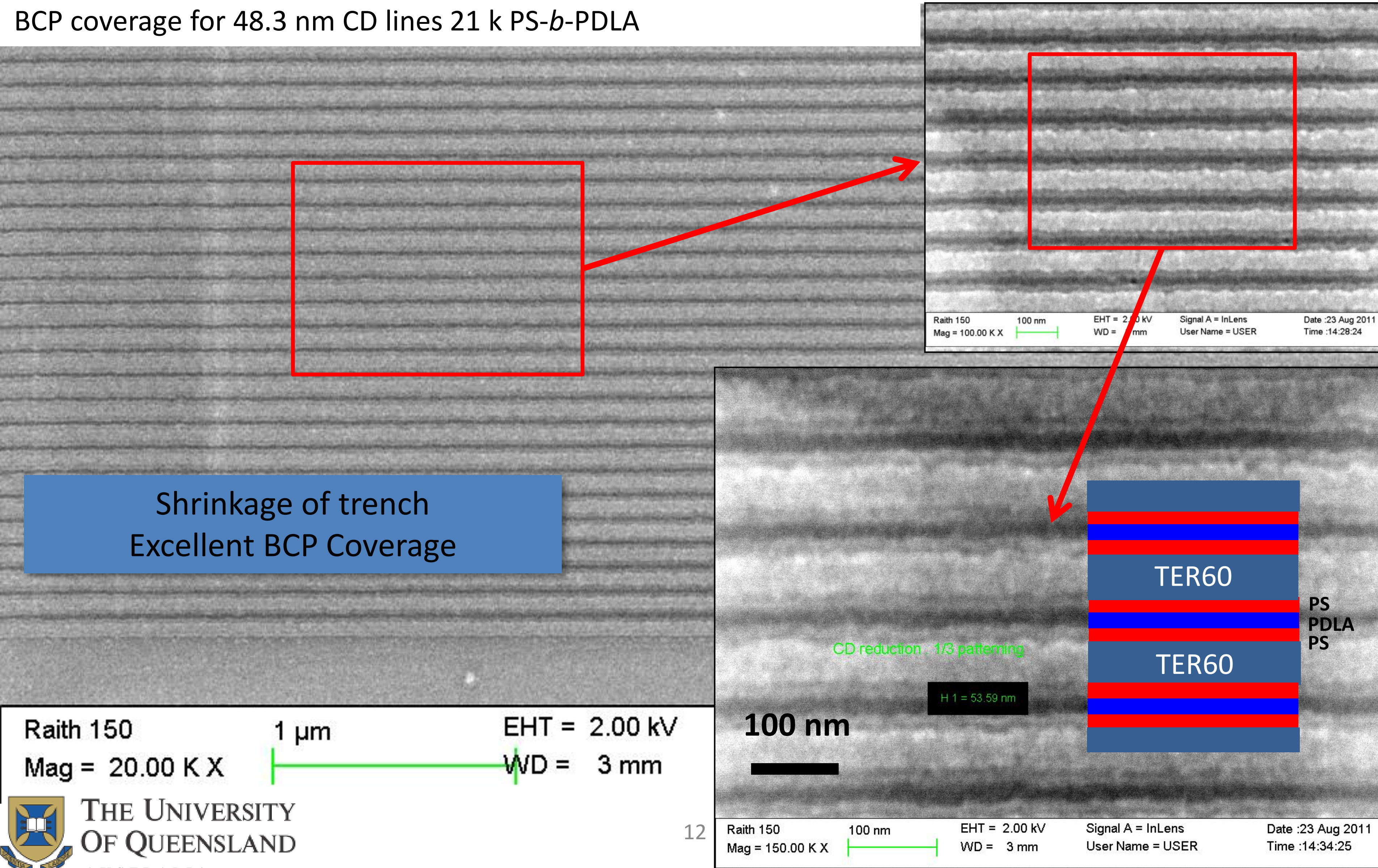


BCP coating conditions
- 1.5 wt% PS-PDLA
- 100 °C PAB

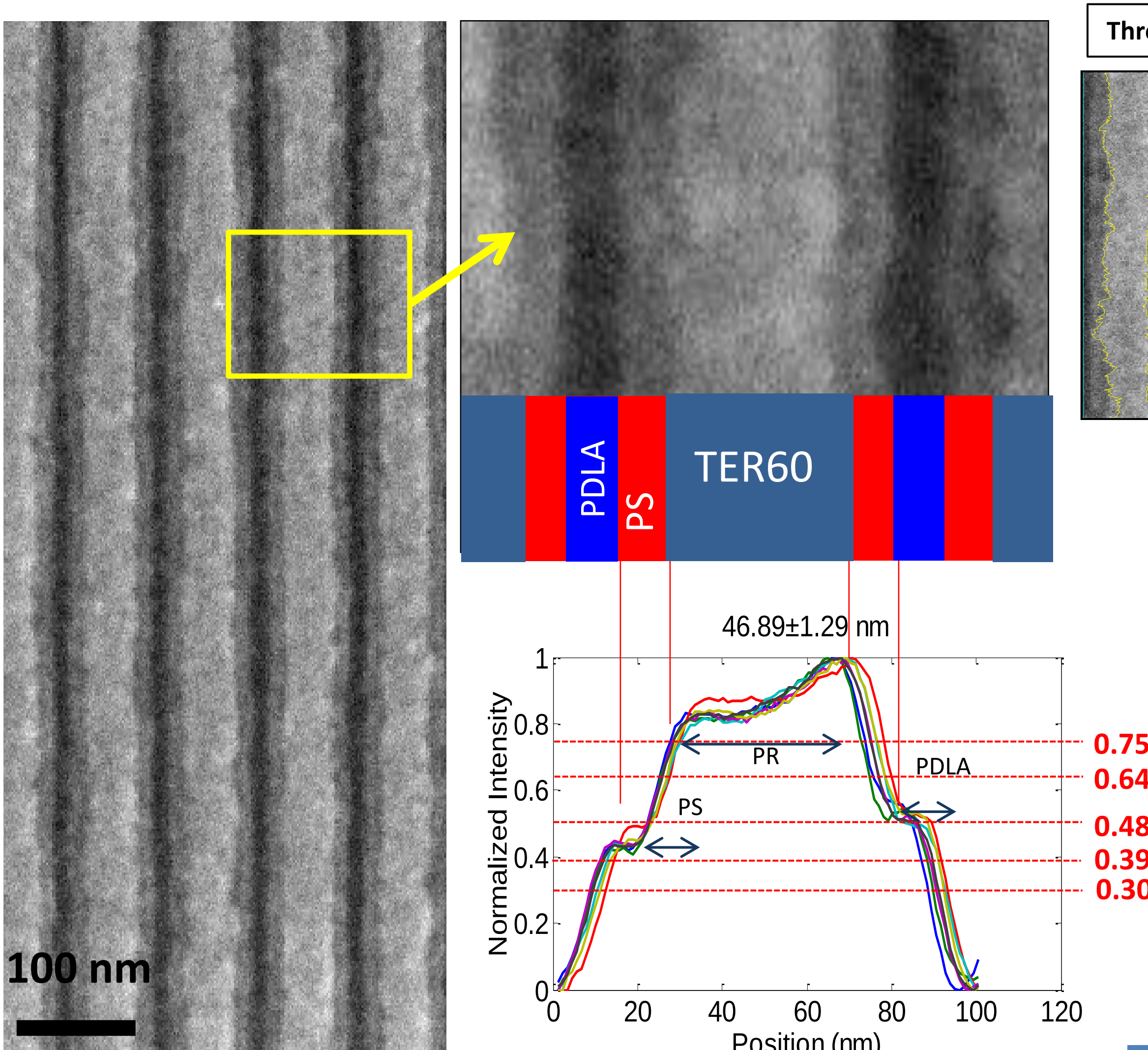
RIE parameters:
Gas: O_2 @ 50 sccm
Pressure: 35 mT
Power: 20 W
Time: 30 s

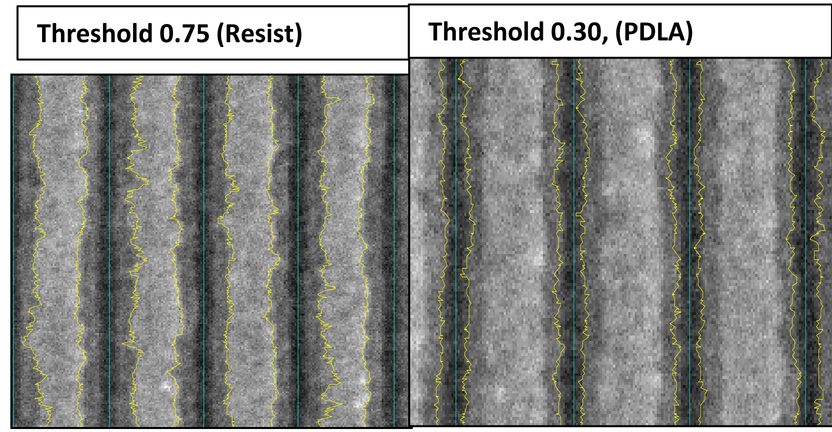
DSA Results (2 L_0)

BCP coverage for 48.3 nm CD lines 21 k PS-*b*-PDLA



LER Analysis





Threshold	CD (nm)	LER (nm)
0.75	45.4	11.0
0.64	51.5	10.6
0.48	63.7	9.0
0.39	71.8	8.1
0.30	79.3	7.6
0.23	84.1	8.3

30% reduction in LER observed

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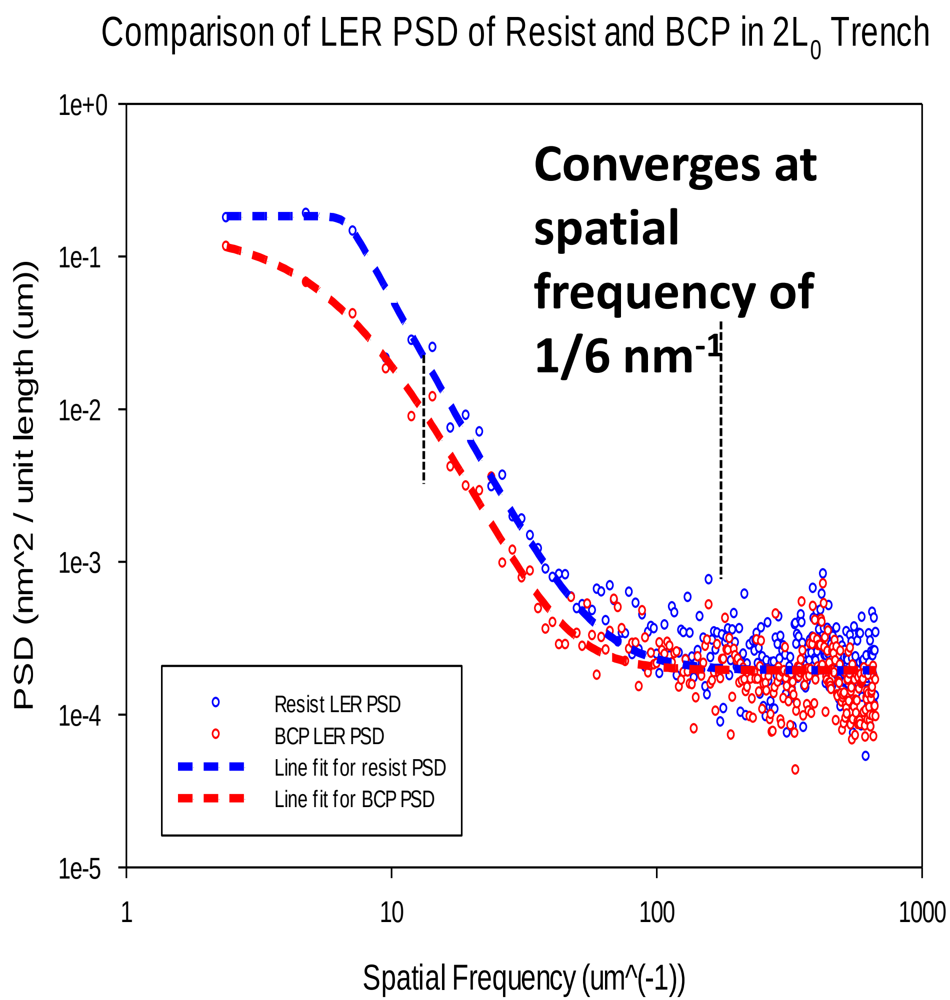
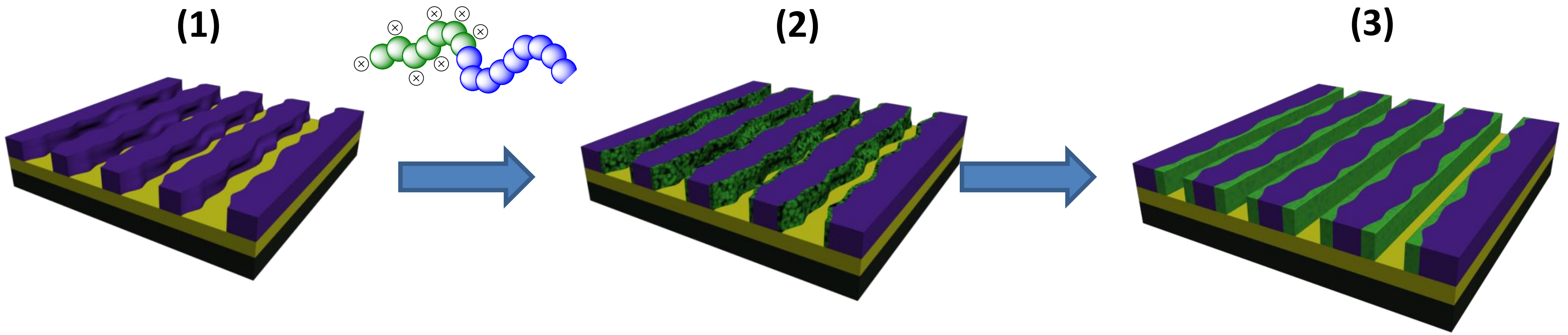
LER analysis - PSD



- PSD is significantly lower at lower frequency ranges (~1/70 nm^{-1} to 1/333 nm^{-1})
- Converges at a spatial frequency of ~1/6 nm^{-1}

Concept 2

Overview of Methodology



1) Sidewalls of non-CAR resists are typically negatively charged.
2) Allows attachment of positively charged block copolymers.
3) Annealing at temperatures above T_g of non-charged block allows polymer to re-arrange to reduce LER.

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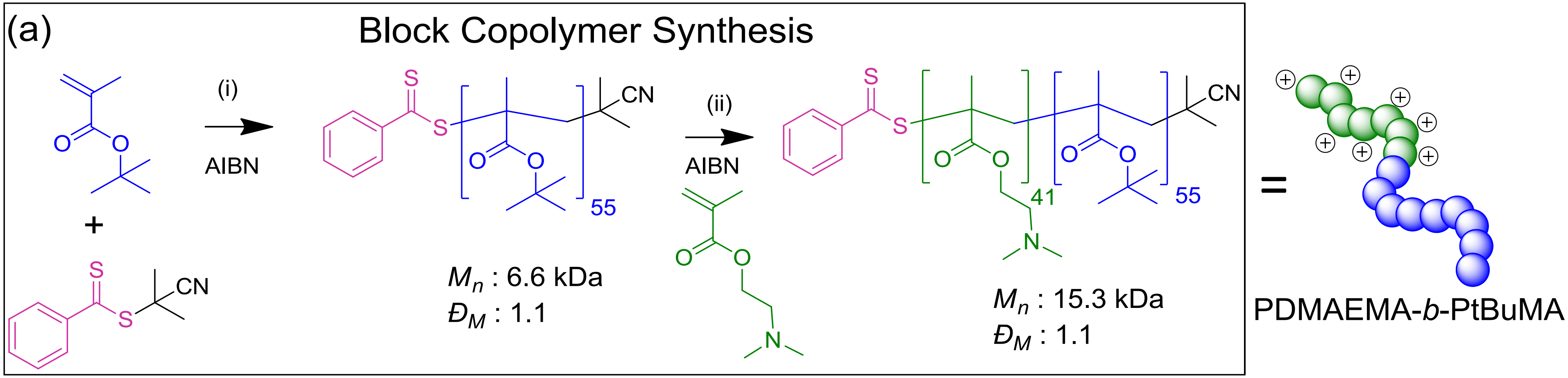
Preparation of block copolymer

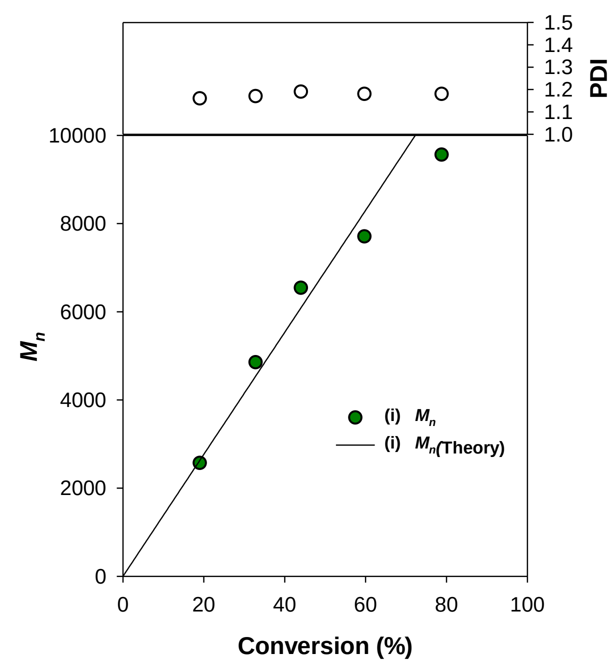


- Use controlled polymerization (RAFT) so get controlled size (M_n) and dispersity of size (PDI).
- <u>Design philosophy</u>

  - PDMAEMA imparts charge and water solubility.

  - PtBuMA : intermediate T_g facilitates healing during annealing and is hydrophobic to drive self assembly of nanostructures in water.

Control of size



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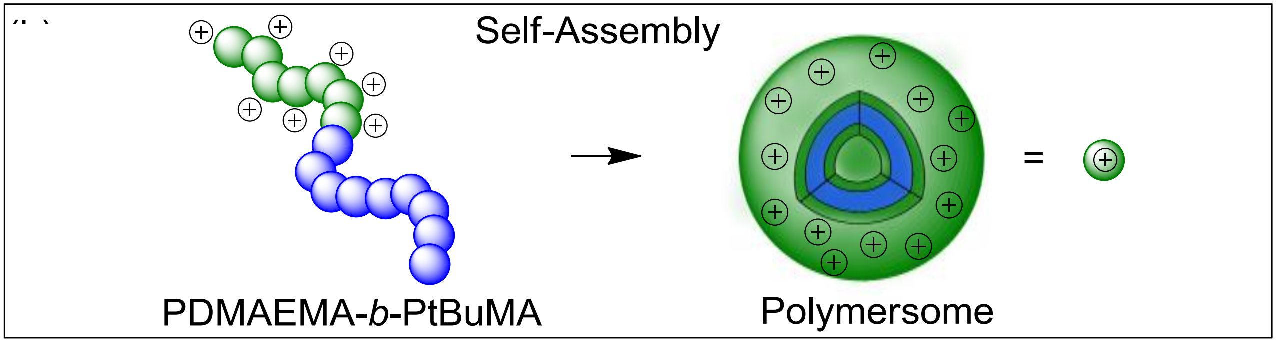
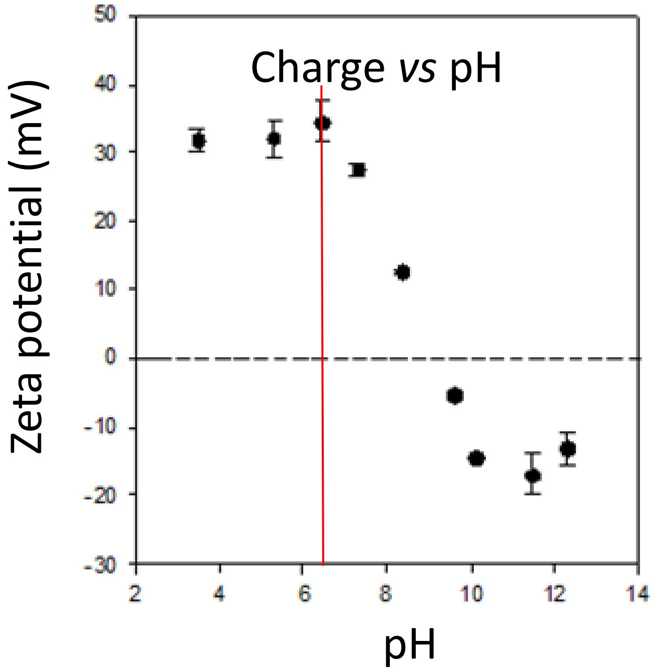
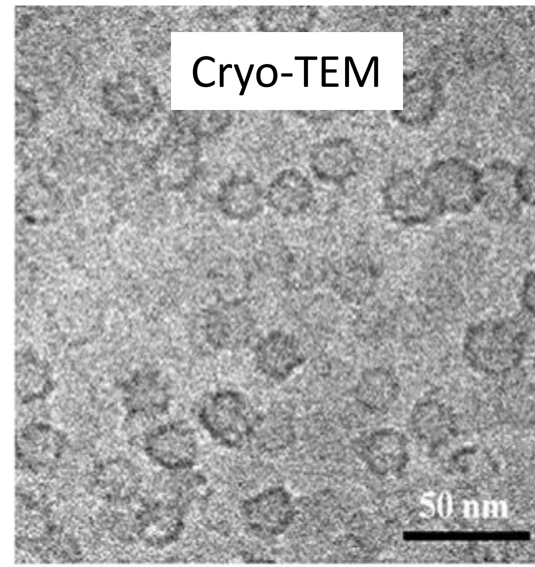
Block copolymer self assembly in water







- Charge of BCP is *pH* dependent and plateaus at pH values < 6.5
- At this *pH* 6.3, the cryo-TEM shows the BCP forms polymersomes (vesicles).

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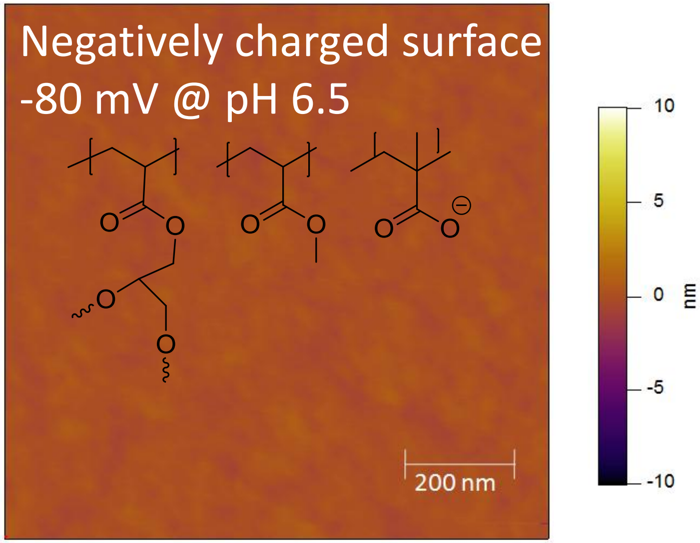
Australia

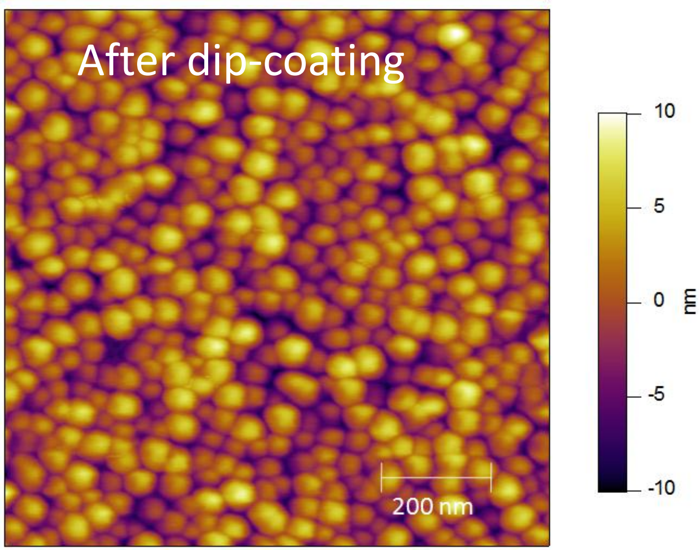
Adhesion to negatively charged surfaces

AFM analysis

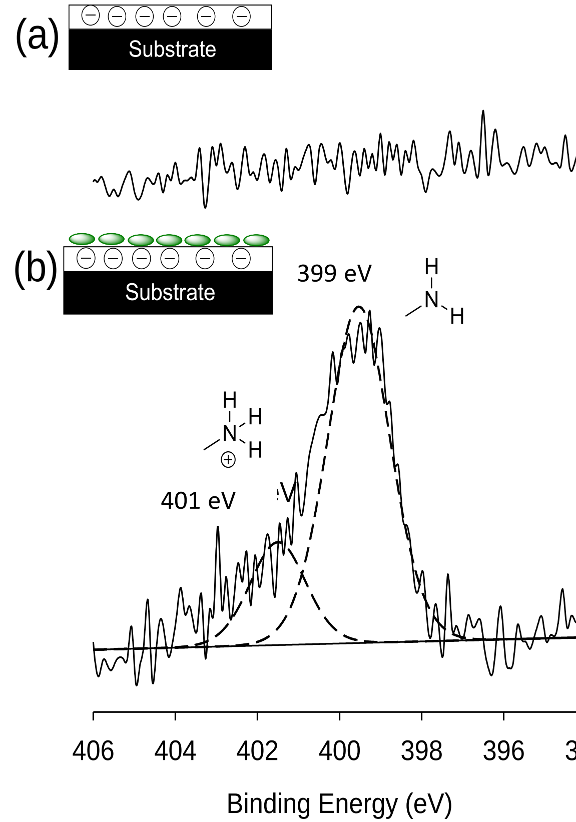
Before coating



After coating



XPS analysis (N 1s)



- Adhesion of positively charged polymersomes onto negatively charged surfaces is confirmed.

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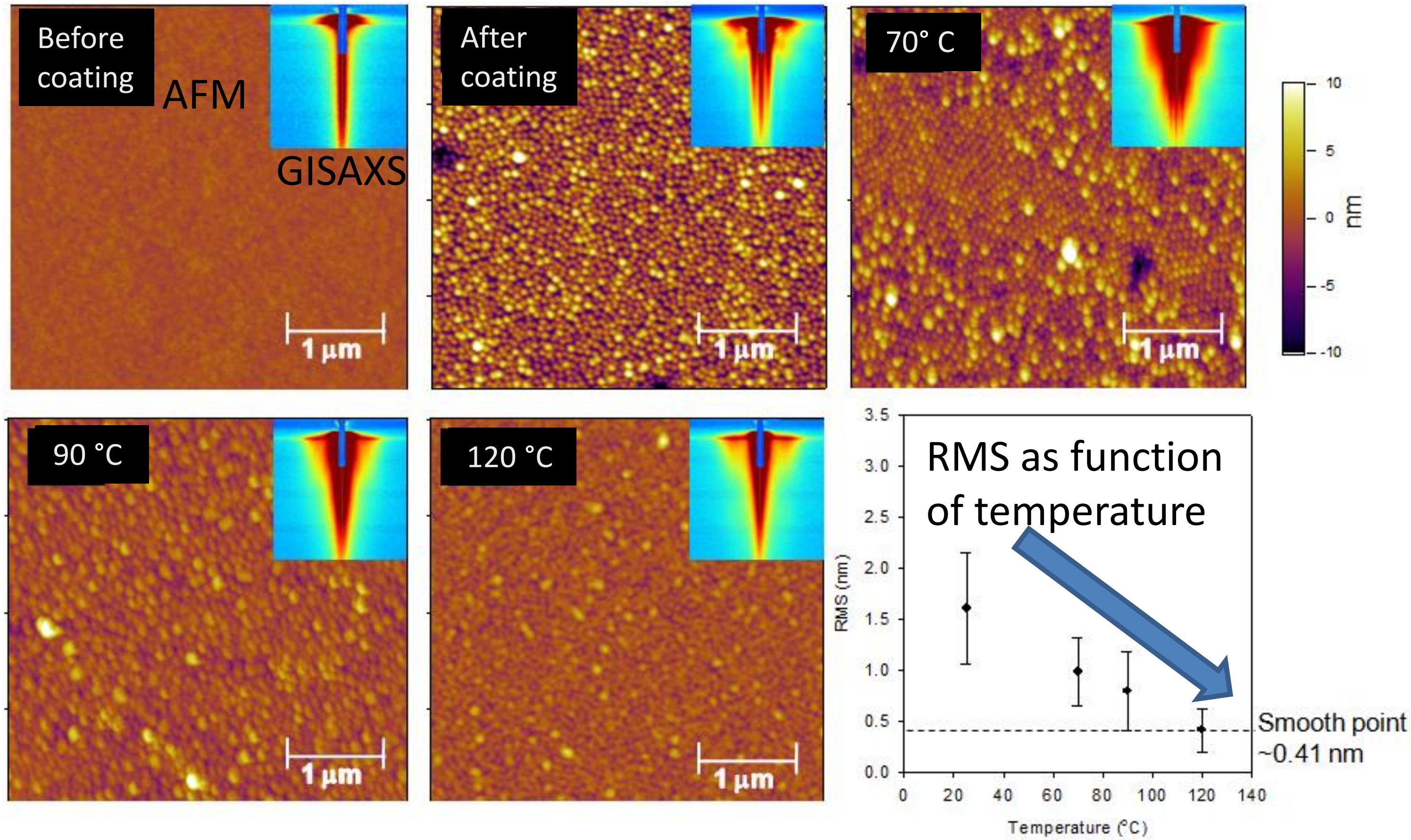
Effect of annealing



- AFM - Decrease of surface roughness with increasing temperature.
  - BCP rearranges → smoother surfaces driven by minimization of surface tension.
- GISAXS - Bragg rods are consistent with deposition of vesicles.
  - Loss of these features during annealing are also consistent with surface restructuring and smoothing.

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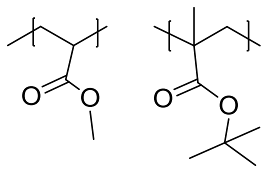
Preparation of model rough surface

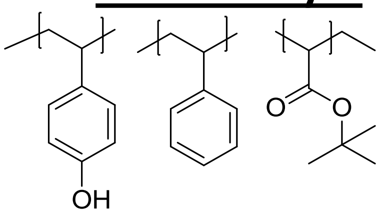
Top Layer



56 mol% : 44 mol%

1 wt% in anisole + PAG

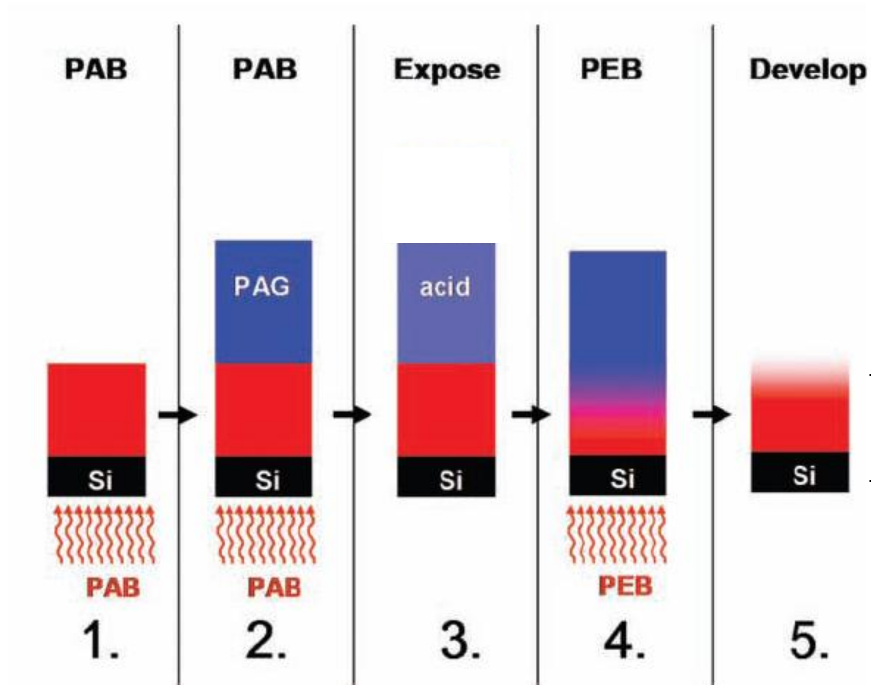
Bottom Layer



60 mol% : 20 mol%: 20 mol%

10 wt% in EL + 0.07 wt% quencher

Prabhu, V.M., et al., Advanced Materials, 2010



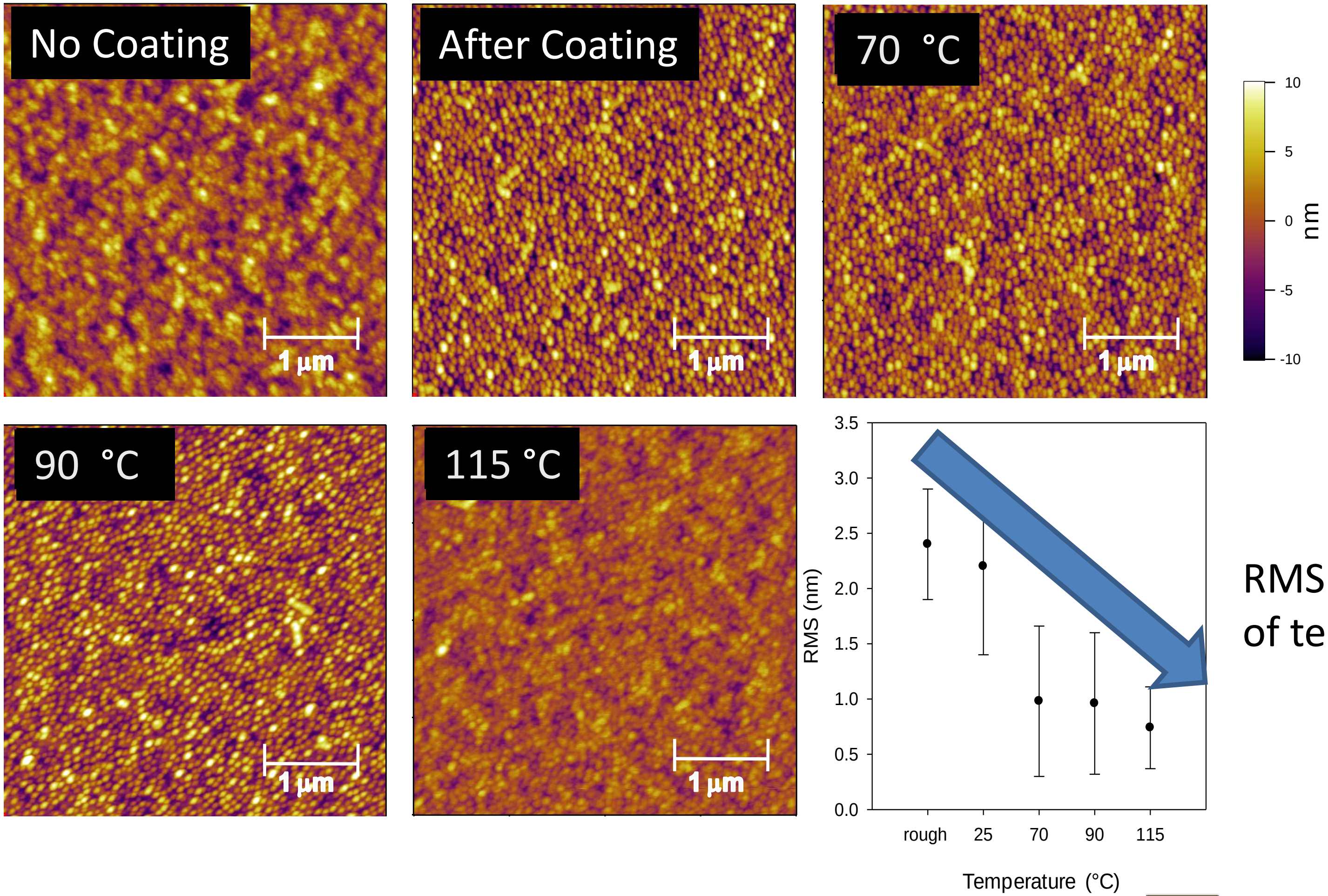
RMS ~2.5 nm & layer thickness is 44 ± 5 nm

Schematic was reproduced from Prabhu, V.M., et al., *Advanced Materials, 2010*

- Bilayer films were prepared with PAG in the top layer, but not in the bottom layer.
- Upon illumination a strong acid will be produced, which diffuses vertically to the bottom layer during PEB.
- This method creates a surface with similar roughness chemistry to the side wall of resist features.

Annealing on model rough surface

AFM



RMS as function of temperature

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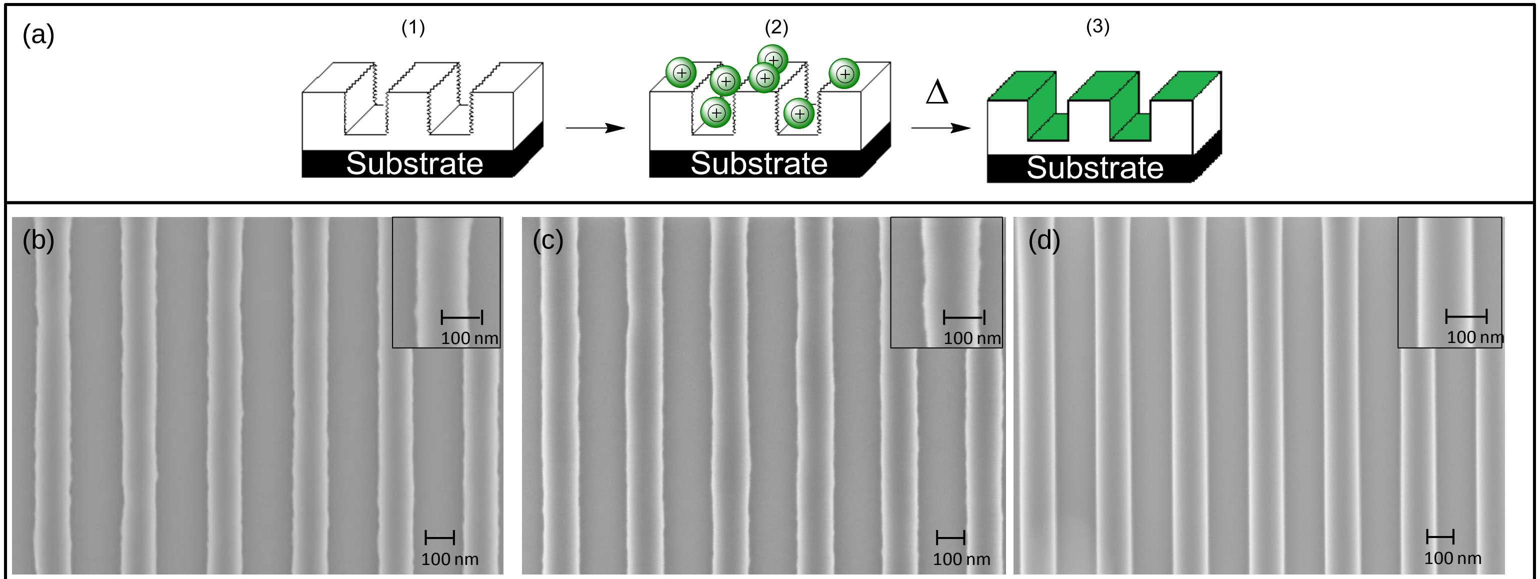
- Roughness was smoothed (healed) upon annealing (from RMS 2.5 to 0.7 nm).
- The annealing temperature > T_g of the BCP, but less than the resist.
- 70% decrease in RMS roughness.

Healing of Patterned Features



CD: 174 nm ± 5 nm
LER : 5.8 nm ± 0.4 nm

CD: 166 nm ± 1 nm
LER : 5.7 nm ± 0.1 nm

CD: 160 nm ± 1 nm
LER : 3.4 nm ± 0.3 nm

- LER before coating - 5.8 nm.
- Dip-coating with polymersomes solution shows a decrease in CD, but LER remains similar.
- Annealed polymersomes on patterned surface can reduce LER from 5.8 nm to 3.4 nm (41 % decrease).

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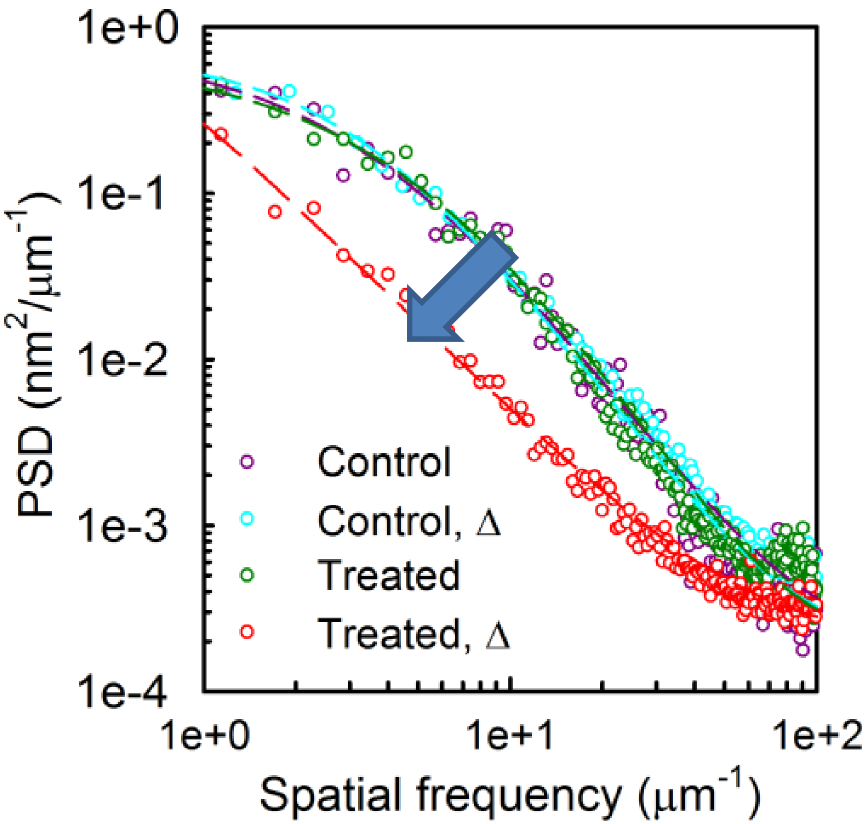
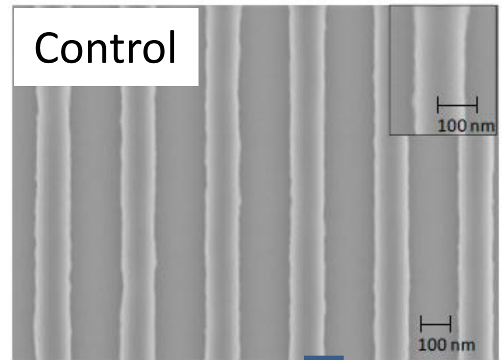
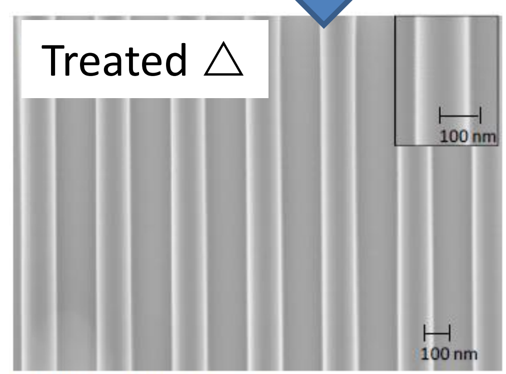
BCP mediated LER Smoothing - PSD





CD: 174 nm ± 5 nm
LER : 5.8 nm ± 0.4 nm



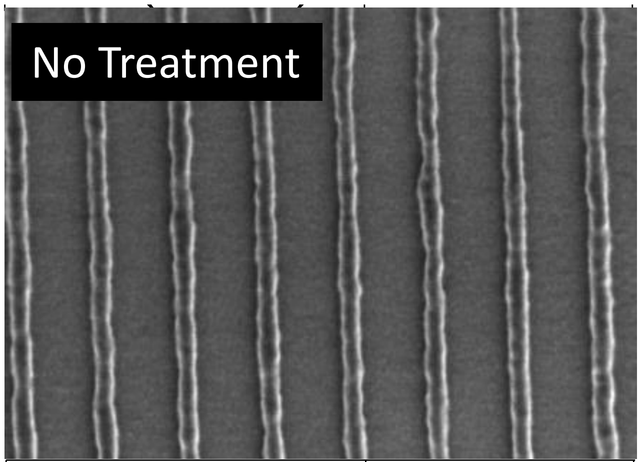
CD: 160 nm ± 1 nm
LER : 3.4 nm ± 0.3 nm

Smoothing observed over all frequency ranges.

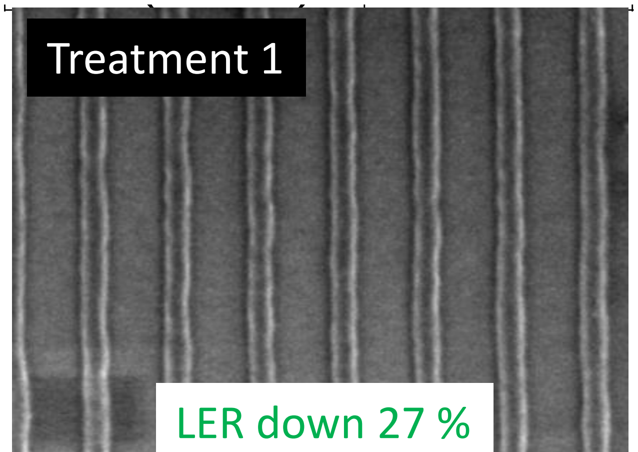
2nd Gen BCPs for Healing

- 1st generation BCPs had a diameter of ~19 nm.
  - Obviously not ideal for healing small features (<40 nm).
- 2nd generation BCPs aim to decrease size of particles (target < 6 nm)

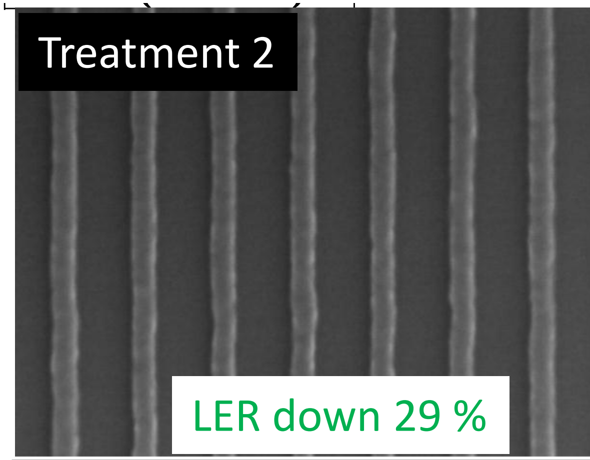
EUVL Patterned Resist – Thanks to Michael Leeson @ Intel. PHOST based resist



CD (Control)	37 ± 1
LER(Control)	5.9 ± 1.1



CD (Control)	47 ± 3
LER(Control)	4.3 ± 0.8



CD (Control)	50 ± 1
LER(Control)	4.2 ± 0.5

More details at SPIE 2013

Conclusions/Summary

1. PS-*b*-PDLA block copolymers are capable of assembling into patterned resists to give half pitch CD as small as 8.0 nm.
   - Polymers with smaller domain sizes are being investigated.
   - T_g of BCP is lower than for typical resist polymers
     - no hardening of resist required.
   - Coating solvent is a non-solvent for a PHOST based resist.
   - Trench shrink of 66% - 48 nm → 16 nm.
   - LER reduction ~30%.

2. Treatment with Aqueous solutions of BCP lead to substantially improved LER and have potential for general use.
   - Champion LER decrease in model rough surface – 70%
   - Champion LER decrease in patterned features – 41%

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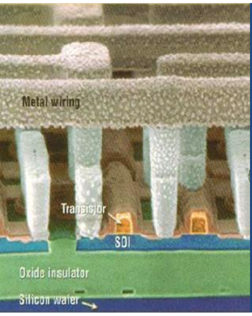
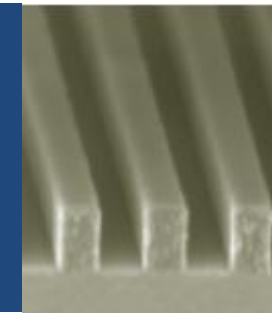


Development of DSA Approaches for Healing of LER and Shrinking of CD that are Compatible with Standard EUV Resists



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